Electrogeneration of the Anion of Ethyl Nitroacetate and Its Use in Electroorganic Synthesis

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Nitroacetic acid and its esters can serve as useful starting points for the synthesis of many classes of substances including esters of 2-nitroalkanoic acids, nitro alcohols, nitroamines, halonitro compounds, di- and trinitro compounds, nitroacrylates, oxazolidines, oxazoles, amino acids, amino alcohols, etc.[2] Typically, the nitro compound is converted to its anion, either in situ or with prior isolation, usually as the sodium or potassium salt. The anions react with alkyl halides, acetates, carbonates, amines, and alcohols or condense with aldehydes, ketones, and imino compounds. The nitronate anions also undergo Michael addition with appropriate acceptors, halogenation, and alkoxymethylation.[3]

Methods for the large-scale preparation of ethyl nitroacetate, 1, have been vastly improved[4] offering promise of its availability in quantity at low cost. With this in mind, it is worthwhile to explore ways to enhance the usefulness of this versatile starting material and to improve the selectivity of its reactions.

Both the solvent and the counterion can affect the rate and selectivity of the reactions of anions such as 2. One means of producing the anion that allows control of solvent and counterion identity is through the production of an electrogenerated base (EGB).[5] Typically, a "probase" is selected that can be reduced at the cathode producing the EGB, which is an anion radical, dianion, or carbanion. The EGB in turn will deprotonate an appropriate starting material, e.g., a weak C–H acid, to produce a carbanion that goes on to react to form the desired products.

In view of the fact that 1 is a relatively strong acid ($pK_a(H_2O)^6 = 5.75$; $pK_a(DMSO)^7 = 9.2$) it is attractive to consider whether the anion 2 can be generated directly at the cathode (eq 1). Similar direct electrogeneration of a variety of organic anions from C–H,[8] N–H,[9] O–H,[10] P–H,[11] and S–H acids[10c,12] has been demonstrated and used as a basis for a number of selective electroorganic syntheses.

$$\underset{\mathbf{1}}{O_2NCH_2COOEt} + e \rightarrow \underset{\mathbf{2}}{O_2N\overset{-}{C}HCOOEt} + {}^1/_2\,H_2 \quad (1)$$

Little is known[13] about the electrochemical properties of 1. It might be expected that electroreduction of 1 in nonaqueous media on a platinum or glassy carbon cathode will proceed via cleavage of the C–H bond and generation of the carbanion as has been observed for other aliphatic mononitro compounds.[14] However, we have found that the reduction of 1 in carefully deoxygenated acetonitrile (AN) is accompanied by cleavage of the C–N bond with elimination of the nitro group as has been found for reduction of ethyl 2-nitroisobutyrate.[15] Cyclic voltammograms obtained after controlled potential electrolysis of 1 ($Pt/0.1\ M\ Bu_4ClO_4/MeCN$, 1 F/mol) at −1.7 V vs AgRE (silver reference electrode) show that 1 has been consumed (absence of reduction peak at −1.82 V) and two large oxidation peaks with approximately equal heights now appear at +0.49 and +0.20 V. The results are almost identical when a glassy carbon electrode is used. The peak at 0.49 V appears at the same potential as observed for the oxidation of 2, prepared independently, while the peak at 0.20 V corresponds to oxidation of nitrite as confirmed by recording a voltammogram of a solution of sodium nitrite.

Evidently, direct reduction of 1 in the absence of oxygen produces a large amount of nitrite ion. It is clear that, at least in the absence of oxygen, the conversion of 1 to 2 is not quantitative, suggesting that direct electrogeneration of 2 for synthesis under these conditions will not be very efficient.

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Table I. Electrochemical Alkylation and Michael Addition of Ethyl Nitroacetate (1)

entries	RX/olefin	condns[a]	charge (F/mol)	product	yield[b] (%)
1	MeI[c]	Et_4NClO_4/MeCN	1.11	**3a**	85
2		Bu_4NBr/MeCN	1.10	**3a**	87
3		Bu_4NClO_4/MeCN	1.09	**3a**	95 (81)
4	$BrCH_2CH_2COOEt$[d]	Et_4NBr/MeCN	1.18	**3b**	93 (81)
5	$BrCH_2CH{=}CH_2$[c]	Et_4NBr/MeCN	1.03	**3c**	93 (80)
6	$PhCH_2Cl$	NaBr-Et_4NBr/DMF	1.02	**3d**	82 (70)
7	$CH_2{=}CHCOOEt$[e]	Bu_4NBr/MeCN	0.15	**3b**	92 (80)
8		Bu_4NClO_4/THF	0.07	**3b**	93 (82)
9	$CH_2{=}CHCN$[e]	Bu_4NBr/MeCN	0.10	**3e**	93 (85)

[a] Electrolyses were carried out under controlled current conditions, in a divided cell, electrolyte concentration 0.25 M (current density 1–2 mA/cm^2) for alkylation and 0.01 M (0.2–0.3 mA/cm^2) for Michael Addition. Platinum gauze cathode and magnesium rod anode. Solutions were air-saturated. [b] Determined by gas chromatography. Isolated yields in parentheses. [c] Ratio 1 to RX 1:2.2. [d] Ratio 1 to RX 1:1.2. [e] Ratio 1 to olefin 1.1:1.

A different behavior was observed when reduction of 1 was carried out in air-saturated AN. Controlled potential electrolysis was carried out at −1.2 V where oxygen (E_p = −1.16 V) is reduced but 1 (E_p = −1.8 V) will not react. One F per mol of 1 was consumed, and the resulting fully electrolyzed solution produced a large anodic peak (E_p = 0.49 V) due to oxidation of 2 with scarcely any nitrite detected. The height of this oxidation peak is 95% that of the original reduction peak for 1 which is consistent with nearly quantitative conversion of 1 to 2, and with the assignment of an overall one-electron oxidation of 2.[16]

Thus, the EGB superoxide efficiently converts 1 to 2. This transformation is successful because oxygen is reduced to superoxide more easily than the reduction of 1 at the electrode. It is known that superoxide is an effective base that can deprotonate organic acids with pK_a as large as approximately 24.[17] When electrolyses are performed in oxygen-saturated solutions, nitronates of secondary nitro compounds have been shown to undergo autoxidation to form ketones.[17b] However, in the case of 1 autoxidation obviously does not proceed (at least in air-saturated solution), making it possible to use 2 as a nucleophile in various synthetic reactions.

Alkylations. Thus, in air-saturated solutions, 2 is efficiently electrogenerated from 1. It is important to remember that by the electrochemical method we can produce almost any salt of 1 in many different solutions simply by changing the electrolyte and solvent. From a synthetic point of view, this capability provides obvious advantages. For example, there is no need to use alkali metals to form the anion or to synthesize alkoxides that are frequently used as bases in synthesis. Also, it is not necessary to isolate explosive salts of nitro compounds (the reactivity of pure salt is higher than reactivity of salt generated by base[3g]). Finally, it is simple to prepare directly in solution tetraalkylammonium salts of 1 whose reactivity is much higher than that of alkali salts.

At first we investigated the alkylation of 1 with alkyl halides. It is known that in the chemical alkylation of 1 the yields of C-alkylated products are low because the process is accompanied by O-alkylation with formation of unstable alkylnitronates.[2,3j] Satisfactory yields are usually possible when the chemical alkylation reaction is carried out in dipolar aprotic solvents (such as DMA and DMF).[3a,b,g]

The results of the reactions of electrogenerated 2 are summarized in Table I. For methylation, the electrolyses were carried out in a divided cell with passage of 1.09–1.11 F/mol at room temperature using tetraalkylammonium salts as electrolyte in AN containing 1 and MeI. Very good yields of methylated product **3a** were obtained with different electrolytes (entries 1–3) but the best result, 81% isolated, was with Bu_4NClO_4 (entry 3). When Et_4NBr was used as electrolyte, poor yields and precipitation of Et_4NI, which is poorly soluble in acetonitrile, were observed indicating that methyl iodide was being converted irreversible to methyl bromide, which is a weaker electrophile and more volatile (bp 3.6 °C) than methyl iodide. But with Bu_4NBr, the yield of **3a** was very good because the solubility of Bu_4NI is much higher and the conversion of MeI to MeBr is reversible.

A very good result was also obtained with the less reactive halide, ethyl 3-bromopropionate. The yield of monoalkylated product **3b** was high (entry 4) even when electrolysis was carried out with Et_4NBr.

For comparison it should be noted that chemical methylation of methyl nitroacetate[3g] produced a yield of 74.5% (methylation of 1 was not reported) and for the synthesis[3a] of **3b** by alkylation of 1, the yield was apparently in the range of 54–72%.

The electrochemical method provides considerable advantage when alkylation of 1 was carried out with allyl bromide giving **3c**. The yield of **3c** by chemical reaction was only 10%[19] while under electrochemical conditions this reaction proceeds with high selectivity (entry 5) giving an isolated yield of **3c** of 80% (chromatographic: 93%) comparable with synthesis of **3c** via π-allylpalladium complexes.[3e]

$$2 + RX \rightarrow \underset{\textbf{3a–d}}{O_2NCHRCOOEt} + X^- \qquad (2)$$

a: R = Me; b: R = CH_2CH_2COOEt;
c: R = $CH_2CH{=}CH_2$; d: R = CH_2Ph

We also demonstrated how we can use an electrosynthesized salt of 1 as a reagent in normal chemical reactions. As an example, the chemical benzylation[3b] of the sodium salt of 1 with benzyl bromide in DMF produces **3d** with a yield of 62% (preparative chromatography). The electrochemical procedure involves electrolysis (1.08 F/mol) of 1 carried out in DMF containing NaBr and Et_4NBr as a mixed electrolyte. Then benzyl chloride was added and the solution was stirred at 60 °C for 5–6 h (the same conditions used in the chemical benzylation[3b]). Isolation by distillation gave a yield of **3d** of 72% (entry 6, Table I).

Michael Addition. It is known that Michael addition reactions are efficiently catalyzed by both EGB[5b,17] and

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Table II. Peak Potentials for the Reduction of Some Nitro Compounds and Oxidation of Their Anions (where Possible)[a]

compds	electrolyte	$E_{p,red}$, V	$E_{p,ox}$, V
1	Bu_4NClO_4/AN	−1.82 (−1.87)[b]	0.494 (0.4)[b]
	Et_4NClO_4/AN		0.519
	Me_4NClO_4/AN		0.530
	$Mg(ClO_4)_2$/DMF		0.693
	$NaClO_4$/AN+10%DMF		0.783
	$LiClO_4$/AN+10%DMF		0.903
	$LiClO_4$/AN		0.972
3a	Et_4NClO_4/AN	−1.91	0.44
4a		−2.01	
3b		−1.86	0.46
4b		−1.92	
5		−1.98	

[a] Electrolyte concentration 0.10 M, platinum disk working electrode. Potentials are referred to silver reference electrode and were determined at scan rate of 0.10 V/s. [b] Potentials measured with glassy carbon working electrode are given in parentheses.

directly electrogenerated anions.[12c] The Michael acceptors ethyl acrylate and acrylonitrile were used to examine addition reactions initiated by electrogenerated anion **2**. As can be seen in eqs 3 and 4, the addition is actually

$$\mathbf{2} + CH_2{=}CHY \rightarrow O_2NC(COOEt)HCH_2\bar{C}HY \quad (3)$$

$$O_2NC(COOEt)HCH_2\bar{C}HY + \mathbf{1} \rightarrow \underset{\mathbf{3b,e}}{O_2NCHRCOOEt} + \mathbf{2} \quad (4)$$

R = CH_2CH_2Y; **b**: Y = COOEt; **e**: Y = CN

catalytic, with the anion initially formed by addition to olefin (eq 3) subsequently deprotonating the nitroacetic ester **1**, hence regenerating the anion **2**.

Excellent yields of **3b** and **3e** (Table I, entries 7–9) were produced by controlling the relative amount of olefin and the quantity of electricity passed. The catalytic nature of the process is illustrated by the production of 82% isolated **3b** in THF solvent with the passage of only 0.07 F/mol (entry 8). Once again the yield in the electrochemical reaction was higher than achieved chemically, 55% for **3b**[3h] and 52–75% for **3e**.[23–24]

Alkylations and Michael Addition of Some Derivatives of Ethyl Nitroacetate. Our electrochemical method can easily be extended to generate the anion of any nitroacetate derivative that has an activated CH bond.

The peak potentials for the irreversible reduction of some of the nitro compounds encountered in this work along with the potentials for oxidation of their anions (where possible) are summarized in Table II.

It has been shown[18] that there is a good correlation between the nucleophilic reactivity of anions and the half-wave potential for their oxidation with the most positive potentials being associated with the weakest nucleophilicity. From the data of Table II we can see that the oxidation potential of anions of **3a** and **3b** is lower than that of **2**. Therefore, we can expect that nucleophilic reactivity of anions of alkylated derivatives of **1** (**3a** and **3b**) will be higher than the reactivity of **2** and reactions of these compounds should proceed with no problem. As we can see from the data of Table III, the alkylation (eqs 5–6) and Michael addition reactions (eqs 7–9) of these derivatives were quite effective and very good yields of isolated products were obtained.

Table III. Electrochemical Alkylation and Michael Addition of Some Derivatives of Ethyl Nitroacetate

entries	compds[a]	RX/olefin	charge (F/mol)	product	yield[b] (%)
10	**3a**	MeI[c]	1.10	**4a**	92 (75)
11		$BrCH_2CH_2COOEt$[d]	1.11	**5**	95 (88)
12		$CH_2{=}CHCOOEt$[e]	0.15	**5**	94 (85)
13	**3b**	MeI[c]	1.13	**5**	90 (78)
14		$BrCH_2CH_2COOEt$[d]	1.15	**4b**	96 (87)
15		$CH_2{=}CHCOOEt$[e]	0.16	**4b**	95 (84)
16	**3e**	$CH_2{=}CHCN$[e]	0.11	**4e**	93 (82)

[a] Electrolyses were carried out in a divided cell under controlled current conditions with current density 1–2 mA/cm² for alkylation and 0.2–0.3 mA/cm² for Michael Addition. Platinum gauze cathode and magnesium rod anode. Solutions were air-saturated. [b] Determined by gas chromatography. Isolated yields in parentheses. [c] Ratio nitro compound to RX 1:2.2. Electrolyte 0.25 M Bu_4ClO_4/MeCN. [d] Ratio nitro compound to RX 1:1.1. Electrolyte 0.25 M Bu_4NBr/MeCN. [e] Ratio nitro compound to olefin 1:1. Electrolyte 0.01 M Bu_4NBr/MeCN.

$$\mathbf{3a,b} + EGB \rightarrow O_2N\bar{C}RCOOEt \quad (5)$$

$$O_2N\bar{C}RCOOEt + RX \rightarrow \underset{\mathbf{4a,b}}{O_2NCR_2COOEt} + X^- \quad (6)$$

a: R = Me; **b**: R = CH_2CH_2COOEt

$$\mathbf{3b,e} + EGB \rightarrow O_2N\bar{C}RCOOEt \quad (7)$$

$$O_2N\bar{C}RCOOEt + CH_2{=}CHY \rightarrow O_2NC(COOEt)RCH_2\bar{C}HY \quad (8)$$

$$O_2NC(COOEt)RCH_2\bar{C}HY + \mathbf{3b,e} \rightarrow \underset{\mathbf{4b,e}}{O_2NCR_2COOEt} + O_2N\bar{C}RCOOEt \quad (9)$$

R = CH_2CH_2Y; **b**: Y = COOEt; **e**: Y = CN

Electrosynthesis of Disubstituted Derivatives of Ethyl Nitroacetate in One-Pot Reactions. When symmetrically disubstituted derivatives of **1** are desired, it is possible to prepare them directly in a one-pot reaction. In general, the reaction conditions are the same as those used for synthesis of monosubstituted products. The only differences are in the ratio of reagents and the quantity of charge passed. The results obtained are given in Table IV where it may be seen that both alkylation reactions and Michael additions gave disubstituted products with good to excellent yields.

For comparison it should be noted that in the chemical version of Michael addition the yields for **4b**[3h] and **4e**[23] were 68 and 70%, respectively. In the literature there are no data about synthesis of disubstituted derivatives by dialkylation.

In principle, it is possible to carry out electrochemical alkylation and Michael addition in a simpler way using an undivided cell with a sacrificial magnesium anode. However, in this case one must use a solvent that will dissolve the magnesium salt of **1**. As an example we used DMF for the dialkylation of **1** with ethyl 3-bromopropionate and Michael addition to ethyl acrylate. After isolation the yields of **4b** were 55% for alkylation and 59% by Michael addition. The lower yield in the undivided electrolysis

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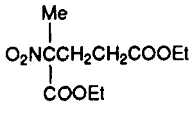
Table IV. Electrochemical Synthesis of Disubstituted Derivatives of Ethyl Nitroacetate in a One-Pot Reaction

entries	RX/olefin	condns[a]	charge (F/mol)	product	yield[b] (%)
17	MeI[c]	$Bu_4NBr/MeCN$	2.11	**4a**	80
18		$Bu_4NClO_4/MeCN$	2.08	**4a**	82 (67)
19	$BrCH_2CH_2COOEt$[d]	$Et_4NBr/MeCN$	2.16	**4b**	89 (80)
20		Et_4NBr/DMF	2.15	**4b**	92 (82)
21	$ClCH_2CH_2COOEt$[d]	$Et_4NBr/MeCN$	2.15	**4b**	81 (72)
22		$Bu_4NBr/MeCN$	2.11	**4b**	85 (78)
23	$CH_2{=}CHCOOEt$[e]	$Bu_4NBr/MeCN$	0.29	**4b**	91 (81)
24		Bu_4NClO_4/THF	0.15	**4b**	(90)
25		Et_4NBr/DMF	0.50	**4b**	81 (70)
26	$CH_2{=}CHCN$[e]	$Bu_4NBr/MeCN$	0.20	**4e**	(91)
27	$MeI/CH_2{=}CHCOOEt$	$Bu_4NClO_4/MeCN$	1.22	**5**	86 (74)

[a] Electrolyses were carried out under controlled current conditions, 1–2 mA/cm^2, in a divided cell, electrolyte concentration 0.25 M (current density 1–2 mA/cm^2) for alkylation and 0.01 M (0.2–0.3 mA/cm^2) for Michael Addition. Platinum gauze cathode and magnesium rod anode. Solutions were air-saturated. [b] Determined by gas chromatography. Isolated yields in parentheses. [c] Ratio 1 to RX 1:2.2. [d] Ratio 1 to RX 1:2.1. [e] Ratio 1 to olefin 1:2.1.

obviously is caused by the low reactivity (see below) of the magnesium salt compared with tetraalkylammonium salts of **1**.

Synthesis of Unsymmetrically Dialkylated Derivatives of Ethyl Nitroacetate. As an illustrative example, we will describe two preparations of diethyl 2-methyl-2-nitroglutarate, **5**. In the first, monoalkylation of ethyl nitroacetate with ethyl 3-bromopropionate was carried out in the most efficient way (Table I, entry 4) with isolation of the product, diethyl 2-nitroglutarate, **3b**. In turn, **3b** was methylated with CH_3I (0.25 M Bu_4NClO_4/CH_3CN) giving a 90% yield (78% isolated) of **5** (Table III, entry 13). The overall isolated yield in the two-step synthesis was 63%.



$$O_2N\overset{Me}{\underset{COOEt}{C}}CH_2CH_2COOEt$$

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Secondly, monoalkylation of **1** with methyl iodide was carried out in 0.25 M Bu_4NClO_4/CH_3CN (conditions of entry 3, Table I) followed by the addition of ethyl acrylate (1.1 mol ratio) and subsequent electrolysis to achieve Michael addition and the production of **5**. The yield in this one-pot synthesis was 86% (74% isolated).

By using AN as solvent and tetralkylammonium cations that do not tend to form ion pairs, very high nucleophilic reactivity of anion **2** is realized. As pointed out earlier, there is an excellent correlation between oxidation potential and nucleophilic reactivity. From the data of Table II we can see that the oxidation potential of anion **2** decreases along the series $Li^+ > Na^+ > Mg^{2+} >$ tetramethyl- > tetraethyl- > tetrabutylammonium cation so it is expected that nucleophilic reactivity of **2** will increase in the same order. Therefore, electrochemical alkylation and Michael addition of **1** and derivatives of **1** can be carried out at room temperature with tetraalkylammonium salts. Under the electrolysis conditions, electrochemically generated **2** was able to displace iodide, bromide, and even chloride (Table IV, entries 21 and 22) from organohalides of various structures. Due to the mild conditions of the process (room temperature and absence of any base), the method should allow synthesis of a wide variety of nitroacetic acid esters, even those that are unstable in alkaline media.

The use of EGB overcomes a difficulty that is often encountered in electrosynthetic practice, viz. further reduction of the reaction products at the cathode. As can be seen from Table II, **1** and its mono- and dialkylated derivatives have similar reduction potentials, but oxygen is reduced ($E_p = -1.16$ V) at a much lower potential than these desired products so the use of superoxide EGB is successful. It should be noted that pure oxygen is usually used for generation of superoxide[5c,17b] as EGB so the electrolysis is carried out under an oxygen atmosphere. In this study the viability of using oxygen from air has been demonstrated whereby electrolyses were carried out simply in air-saturated solution.

In summary, both mono- and dialkylation of ethyl nitroacetate, **1**, have been carried out electrochemically through generation of the anion, **2**, followed by nucleophilic attack on alkyl halides (X = Cl, Br, I) or Michael addition. Synthesis of an unsymmetrically dialkylated ethyl nitroacetate was achieved by two routes, sequential electrolyses with isolation of the intermediate and an attractive one-pot procedure. The electrochemical technique permits simple control of solvent and counterion, two factors that have been shown to affect the rate and selectivity of the reactions of the electrogenerated anions. These studies illustrate some of the capabilities of electroorganic syntheses and very simple, and readily available apparatus (see Experimental Section) have been employed in order to encourage wider use of this synthetic methodology.

Experimental Section

Reagents. Acetonitrile (Fisher), DMF (Burdick and Jackson), THF (Fisher), tetraethylammonium and tetrabutylammonium bromides (Aldrich), tetrabutylammonium (Kodak), tetraethylammonium (G. Frederick Smith) and magnesium perchlorates (Aldrich), sodium nitrite (Fisher), alkyl halides (Aldrich), and ethyl acrylate and acrylonitrile (Aldrich) were used directly as commercially available materials. Tetramethylammonium perchlorate was prepared by the same method that has been described.[20] Ethyl nitroacetate and standard samples of diethyl α-nitroglutarate (**3b**) and diethyl γ-carbethoxy-γ-nitropimelate (**4b**) were obtained from the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow. Standard samples of ethyl 2-nitropropionate (**3a**), ethyl 2-methyl-2-nitropropionate (**4a**), ethyl 2-nitro-4-pentenoate (**3c**), ethyl 3-phenyl-2-nitropropionate (**3d**), ethyl 4-cyano-2-nitrobutyrate (**3e**), and ethyl 4-cyano-2-(2-cyanoethyl)-2-nitrobutyrate (**4e**) were prepared as described elsewhere.[3b,19,21-23]

A solution of the tetrabutylammonium salt of ethyl nitroacetate was prepared by the treatment of an acetonitrile solution of

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(20) Kolthoff, I. M.; Coetzee, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 870.

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(22) Emmons, W. D.; Freeman, J. P. *J. Am. Chem. Soc.* **1955**, *77*, 4391.

nitroacetate with equimolar quantity of 40 wt % tetrabutylammonium hydroxide (Aldrich). The solution was stirred for 10 h at room temperature and dried with alumina.

Instrumentation. Voltammetric measurements and controlled potential electrolyses were carried out in a glass cell. The working electrodes were platinum (2.18 10^{-2} cm^2) or glassy carbon (7.07 10^{-2} cm^2) disk electrodes for cyclic voltammograms (scan rate 0.1 v/s) and a platinum gauze electrode (ca. 10 cm^2) for electrolyses. The electrolyte concentration was 0.10 M, and the volume of the test solution was 10 mL. The auxiliary electrode (platinum wire) compartment was separated from the working electrode compartment by two medium-porosity glass frits. The experiments were conducted using an EG & G Princeton Applied Research (PAR) Model 273 potentiostat/galvanostat. The silver reference electrode was composed of a silver wire in contact with 0.01 M $AgNO_3$, 0.10 M Et_4NClO_4, and acetonitrile, and its potential was 90 mV negative of the ferrocene/ferrocenium couple in acetonitrile.

All electrosyntheses were conducted with manually controlled current using a Kepco Power Supply (0–100 V, 0–5 A), and the charge passed was monitored with an Electrosynthesis 640 digital coulometer.

Gas chromatographic analysis of the nitro compounds was carried out with a Varian Model 3700 gas chromatograph with a 10% OV 101 Chrom GHP 100/120 0.5-m × $^1/_8$-in. column and helium as carrier gas. The column temperature for analysis of **3a** and **4a** was 60 °C for 1 min followed by a 25 °C/min increase to 80 °C; for all other compounds it was 90 °C for 1 min followed by an 80 °C/min increase to 250 °C. A thermal conductivity detector was used at 250 °C. A working curve (peak height vs concentration) was prepared by using solutions of known concentration of standard nitro compounds in AN or DMF. Analysis was performed by direct injection of the electrolyzed solution.

^{1}H NMR spectra were recorded in *d*-chloroform (TMS) solution using a Bruker WM 250 spectrometer.

Cells for Electrosynthesis. The cell for divided electrolyses was a 100-mL glass beaker with a polyethylene cover in which was fixed a platinum gauze cathode (35 cm^2) and the anode compartment which was a polypropylene tube (Nalgene Centrifuge Tube, 28.7 × 103 mm). About 50 6-mm-diameter holes were drilled in the side of the tube, and it was wrapped with three layers of tracing paper to serve as separator (diaphragm). Keuffel and Esser Albanene tracing paper was used but it is likely that any hard, 100% rag paper would be suitable. The paper was held in place by a few rounds of cotton thread. The anode was a 6-mm-diameter magnesium rod.

The cell for undivided electrolyses was a glass vial with a diameter of 25 mm and a height of 52 mm. The platinum gauze cathode (ca. 10 cm^2) and magnesium rod anode (6-mm diameter (Aldrich)) were coaxially fixed on a polyethylene cover.

General Procedure for Preparative Electrolysis. For divided electrolysis a 0.25 M solution (40 mL) of electrolyte in AN or DMF containing 3–10 mmol of **1** and organo halides or olefin (mol ratio 1.0–2.2) was placed in the cathode compartment of the divided cell. In the anode compartment was placed 30 mL of supporting electrolyte.

For undivided electrolysis a 0.01 M solution (10 mL) of electrolyte in AN or DMF containing 3–4 mmol of **1** and organo halides or olefin (mole ratio 1.1–2.2) was placed in the cell.

Electrolyses were performed at room temperature with a current density of 1–2 mA/cm^2 for alkylation and 0.2–0.3 mA/cm^2 for Michael addition. The solution was stirred with a magnetic stirrer and was in contact with the air of the laboratory.

After electrolysis the solution was removed, and the solvent (AN, THF) was evaporated. In the case of DMF, the solution was poured into a saturated aqueous solution of NaCl. The residue or aqueous solution was extracted with ether (5 × 25 mL), the organic layer was washed with 25 mL of 5% sodium hydroxide (only for **4a,b,e** and **5**) and water (3 × 25 mL), and dried (Na_2SO_4). The solvent was evaporated, and the combined residue from three identical electrolyses was distilled.

In entry 6 (Table I) the electrolyte was 0.15 M NaBr + 0.15 M Et_4NBr in DMF. Benzyl chloride was added after electrolysis of **1**, and the solution was stirred at 60 °C for 6 h.

In entries 7–9 (Table I), 15, 16 (Table III), and 23–27 the reaction mixture after electrolysis was stirred for 6 h at room temperature.

In entries 21–22 (Table III) after electrolysis the reaction mixture was stirred 16–20 h at room temperature.

The structure of the products was confirmed by gas chromatography (comparison of retention time with standards), ^{1}H NMR, and by comparison of their boiling or melting points with literature data.

Ethyl 2-nitropropionate (3a): bp 38 °C/0.3 mmHg (lit.[21] bp 55 °C/1 mmHg); ^{1}H NMR (ppm) 0.98 (t, 3 H, J = 7 Hz), 1.48 (d, 3 H, J = 7 Hz), 3.98 (q, 2 H, J = 7 Hz), 4.90 (q, 1 H, J = 7 Hz).

Diethyl α-nitroglutarate (3b): bp 133–136 °C/3 mmHg (lit.[3h] bp 109–112 °C/1 mmHg); ^{1}H NMR (ppm) 1.24 (t, 3 H, J = 7 Hz), 1.27 (t, 3 H, J = 7 Hz), 2.37–2.60 (m, 4 H), 4.14 (q, 2 H, J = 7 Hz), 4.28 (q, 2 H, J = 7 Hz), 5.23–5.33 (m, 1 H).

Ethyl 2-nitro-4-pentenoate (3c): bp 59–61 °C/0.7 mmHg (lit.[19] bp 67–69 °C/2 mmHg); ^{1}H NMR (ppm) 0.99 (t, 3 H, J = 7 Hz), 2.50–2.75 (m, 2 H), 3.97 (q, 2 H, J = 7 Hz), 4.80–4.95 (m, 3 H), 5.35–5.55 (m, 1 H).

Ethyl 3-phenyl-2-nitropropionate (3d): bp 140–142 °C/0.9 mmHg (lit.[22] bp 88–90 °C/0.02 mmHg); ^{1}H NMR (ppm) 1.27 (t, 3 H, J = 7 Hz), 3.43–3.61 (m, 2 H), 4.27 (q, 2 H, J = 7 Hz), 5.34 (dd, 1 H, J = 9, 6 Hz), 7.19–7.37 (m, 5 H).

Ethyl 4-cyano-2-nitrobutyrate (3e): bp 123–125 °C/0.9 mmHg (lit.[23] bp 146.5–148 °C/4 mmHg); ^{1}H NMR (ppm) 1.30 (t, 3 H, J = 7 Hz), 2.46–2.64 (m, 4 H), 4.30 (q, 2 H, J = 7 Hz), 5.21–5.27 (m, 1 H).

Ethyl 2-methyl-2-nitropropionate (4a): bp 34 °C/0.35 mmHg (lit.[21] bp 46 °C/1 mmHg); ^{1}H NMR (ppm) 1.15 (t, 3 H, J = 7 Hz), 1.82 (s, 6 H), 4.16 (q, 2 H, J = 7 Hz).

Diethyl γ-carbethoxy-γ-nitropimelate (4b): bp 153–154 °C/0.3 mmHg (lit.[3h] bp 181–182 °C/2 mmHg); ^{1}H NMR (ppm) 1.18 (t, 6 H, J = 7 Hz), 1.24 (t, 3 H, J = 7 Hz), 2.25–2.52 (m, 8 H), 4.06 (q, 4 H, J = 7 Hz), 4.22 (q, 2 H, J = 7 Hz).

Ethyl 4-cyano-2-(2-cyanoethyl)-2-nitrobutyrate (4e): mp 51–52 °C (lit.[23] mp 51.9–52.7 °C); ^{1}H NMR 1.34 (t, 3 H, J = 7 Hz), 2.50–2.64 (m, 8 H), 4.37 (q, 2 H, J = 7 Hz).

Diethyl 2-methyl-2-nitroglutarate (5): bp 108–109 °C/0.35 mmHg; ^{1}H NMR (ppm) 1.20 (t, 3 H, J = 7 Hz, ester Me), 1.24 (t, 3 H, J = 7 Hz, ester Me), 1.73 (s, 3 H, Me), 2.28–2.56 (m, 4 H, CH_2CH_2), 4.08 (q, 2 H, J = 7 Hz, CH_3CH_2O), 4.21 (q, 2 H, J = 7 Hz, CH_3CH_2O). Anal. Calcd for $C_{10}H_{17}NO_6$: C, 48.58; H, 6.93; N, 5.67. Found: C, 48.22; H, 7.09; N, 5.57.

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